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THIN-FILM COATINGS BASED ON ZIRCONIUM AND COBALT OXIDES

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Thin-film coatings based on zirconium and cobalt oxides are obtained. It is demonstrated that the properties of the coatings depend on the ratio of oxides in the film, the rotational speed of the substrate, and the firing temperature. Films with a low cobalt content have the highest refractive index value and substantial adhesion.

Glasses with thin-film coatings are acquiring great significance and finding wide applications in various sectors of contemporary science and engineering. The demand for such glasses is growing every year. Numerous researchers in Russia and abroad study the effect of coatings on the physicochemical properties of glass and its optical characteristics [1, 2]. Coatings based on binary and ternary oxide systems are used rather frequently [3, 4]. By varying the ratio of oxides in a film it is possible to significantly improve the required parameters of the glass surface. Therefore, a study of the properties of thin films based on zirconium and cobalt oxides is promising and topical.

Films based on zirconium oxide have a number of valuable properties. They are transparent within a wide wavelength range, have a high refractive index, high thermal stability, chemical resistance, and increased adhesion. Such films are used for coating UV lamp bulbs and window panes. Cobalt-based films have absorption in the visible spectrum range, are resistant to the effect of alkali solutions, but have low adhesion and poor resistance to a mechanical impact. They are used to manufacture resistant electrochromium back-view car mirrors. Variation of the ratio between zirconium and cobalt oxide in the film composition makes it possible to vary such film properties as clarity in the ultraviolet and visible spectrum ranges over a wide interval and to increase film adhesion to different substrates.

The purpose of the present study was to obtain films based on zirconium and cobalt oxides from film-forming solutions (FFS) within the total concentration range and to investigate their structure and properties.

Thin films were obtained by precipitation from alcohol FFS of zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$ and cobalt nitrate $Co(NO_3)_2 \cdot 8H_2O$. The total salt concentration converted to oxides was 0.4 M/liter. The cobalt oxide content in films varied in the range of 0 – 100% (here and elsewhere molar content is indicated). The films were produced on quartz and Polycor substrates by centrifuging with the rotational speed of the substrate equal to 500 – 4000 min^{-1}. Heat treatment was carried out at temperatures of 50 – 800°C. The film structure was studied by x-ray phase analysis (DRON-3M), and adhesion was measured by the sclerometric method (PMT-3). The optimum parameters of the films were investigated on a LÉF-3M laser ellipsometer and a Specord-M40 spectrophotometer.

The main factors influencing the properties of films produced by centrifuging include the ratio between the zirconium and cobalt oxides, the rotational speed of the substrate, and the heat treatment temperature.

For a cobalt oxide content of 20, 60, and 70%, the thickness of the film on glass substrate increases with increasing rotational speed (Table 1).

For other contents of cobalt oxide, the effect of rotational speed on thickness and refractive index is more complex. The refraction index and the thickness of the films produced by precipitation of FFS, as a rule, depend on the properties of the solution, its production conditions, and the ratio of oxides in the film [5, 6], as a consequence of which films with different phase compositions and structures can be formed. Therefore, the existence of several factors impedes a unique interpretation of the effect of the rotational speed on the refraction index and the film thickness.

The properties of obtained films also depend on their phase composition. An x-ray phase analysis of films with a cobalt oxide content up to 50% indicated that, as a consequence of heat treatment at 500°C, a metastable cubic modification of zirconium dioxide is formed. Increase in the cobalt oxide content above 10% leads to the formation of additional Co_2O_3 and the monoclinal modification of ZrO_2. This can be accounted for using the of crystal-chemistry criterion:

$$r_{Co^{2+}} < r_{Zr^{4+}}.$$

Replacement of Zr^{4+} by Co^{2+} decreases the stability of the cubic structure and facilitates the emergence of the

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TABLE 1

Molar content of cobalt oxide, %	Rotational speed, min^{-1}	Refractive index	Film thickness, nm
20	500	1.9785	66.30
	1000	2.0078	81.70
	2000	2.0211	100.22
	3000	1.9789	107.01
	4000	2.0129	132.28
40	1000	2.0116	78.90
	2000	1.8809	95.05
	3000	1.9106	110.50
	4000	1.7313	89.94
60	1000	2.2275	30.60
	2000	1.9907	63.10
	3000	1.9241	82.10
	4000	1.8554	99.40
70	500	2.4203	30.00
	1000	2.0123	62.30
	2000	1.9389	82.70
	3000	1.9927	89.40
	4000	1.8631	94.60
80	500	1.9643	47.10
	1000	2.0816	40.70
	2000	1.8916	80.90
	3000	2.0282	78.40
	4000	2.0768	55.90

TABLE 2

Molar content of cobalt oxide, %	Refractive index		Film thickness, nm		Adhesion, kg/mm^2 (polycor substrate)
	glass substrate	polycor substrate	glass substrate	polycor substrate	
0	2.1600	1.9754	105.0	102.3	69.3
10	2.0875	1.9973	102.5	110.6	56.5
20	2.0211	2.0182	100.2	112.2	56.5
60	1.9907	1.9003	63.08	98.2	31.0
80	1.8916	2.1432	80.92	19.3	28.2

monoclinal structure of ZrO_2. The significant difference in the radii of these ions does not allow for the formation of stable solid solutions, which is the reason for the formation of two oxides within the system.

Table 2 presents the dependence of the adhesion, the refraction index, and the film thickness on the composition of the films on the polycor and glass substrates (firing temperature 500°C, rotational speed 2000 min^{-1}). As the cobalt oxide content in the film grows, the adhesion decreases, since cobalt oxide films have lower adhesion than zirconium oxide films.

Films with a cobalt oxide content exceeding 60% have insignificant adhesion. For films on polycor substrates with a cobalt oxide content up to 20% the refractive index increases, which can be attributed to the formation of a solid solution. With a cobalt oxide content equal to 60%, the refraction index is the lowest, presumably due to the formation of a eutectic. The film thickness is maximum within the solid

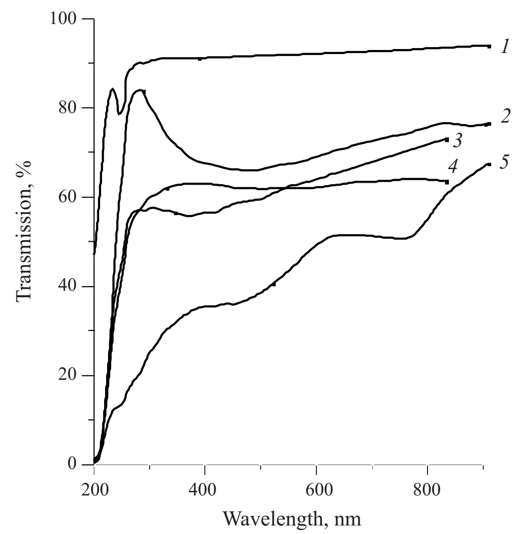

Fig. 1. Transmission spectra of films on quartz substrate: *1*) quartz substrate; *2*, *3*, *4*, and *5*) films made from FFS with the molar content of cobalt nitrate equal to 0, 20, 30, and 50%, respectively.

solution range and decreases as the cobalt oxide content decreases. For films obtained on glass substrates, an increase in the cobalt oxide content decreases the refraction index and the film thickness.

Zirconium oxide films absorb in the wavelength range up to 200 nm, and cobalt oxide films — up to 750 nm. An analysis of the spectra of the films on quartz substrates indicated that as the cobalt oxide content increases, the absorption boundary is shifted to the long-wave range (Fig. 1). The film color in this case changes from clear to dark brown or black. Table 3 indicates the transmission coefficients of the obtained films.

The presence of cobalt oxide has virtually no effect on the absorption of hard UV radiation (204 nm), which results in the formation of ozone in the operation of gas-discharge lamps. At a wavelength of 250 nm, the film transmission coefficient decreases, which impairs the bactericide effect of UV lamps with coatings based on zirconium and cobalt oxides. As the cobalt oxide content increases, the transmission coefficient in the visible spectrum range (714 nm) decreases, which intensifies the sum-shielding effect and makes it possible to use these films as decorative sun-shielding coatings.

Study of the effect of the heat treatment temperature on the film's properties allows some conclusion with respect to

TABLE 3

Molar content of cobalt oxide, %	Transmission coefficient, %, for wavelength, nm		
	204	250	714
0	0.5	63	73
10	1.5	45	68
30	1.5	41	64
50	1.0	14	51

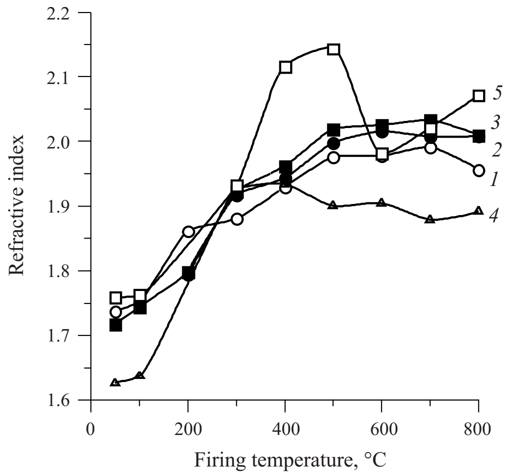

Fig. 2. The refractive index of films depending on the firing temperature for the molar content of cobalt oxide equal to 0 (*1*), 10% (*2*), 20% (*3*), 60% (*4*), and 80% (*5*).

the process of their formation. Figure 2 shows the dependence of the refractive index of films of different compositions on a polycor substrate on the firing temperature. The increase in the refractive index of the films produced at 500°C is related to the formation of an oxide structure in the films [5, 6]. Films containing up to 20% cobalt oxide do not change their refractive index within the temperature interval of 500 – 800°C. This is related to the formation of the cubic structure of ZrO_2, which is stable within the specified temperature interval. The modification of the refractive index of the films with a higher cobalt oxide content can be due to the disintegration of the cubic solid solution and the emergence of the monoclinal modification, as well as release of cobalt oxide. This changes the ratio between zirconium and cobalt oxide and modifies the microstructure and the properties of the films.

Thus, thin films based on zirconium and cobalt oxides have been obtained. Films with a low cobalt oxide content have the highest refractive index and substantial adhesion. For practical purposes it is advisable to use films with a cobalt oxide content up to 60% for coating of UV lamp bulbs and multiple window panes to control the visible light intensity and to give protection from the effect of UV radiation.

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